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CHAPTER XXXI

METALLURGY OF CALCIUM.

Source: Metallurgiya legkikh metallov, Metallurgizdat,  
pp. 532-537 (Ch. XXXI)

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METALLURGY OF CALCIUM

113 - Properties of Calcium and its Application

Calcium belongs to a group of alkaline earth metals (Ca, Ba, Sr) and industrially is the most significant among them. (P. Bassin, Rev. d. alum. No. 99, 1938; C. Mantell, Metals and Alloys No. 2, 1939.) Its specific weight at room temperature (20 degrees Centigrade) is 1.542; thus metallic calcium is lighter than beryllium, magnesium and aluminum.

Table 85 shows the basic properties of metallic calcium:

TABLE 85

Properties of Calcium

<u>Characteristics</u>	<u>Value</u>
Atomic weight	40.07
Valence	2
Specific gravity (20 degrees Centigrade)	1.542
Melting point, degrees Centigrade	810
Boiling point, degrees Centigrade	1170
Electrical conductivity in percentage of silver	
conductivity	45.1
Electrical resistance at 0 degrees, ohms per cubic centimeter	3.43
Specific heat from 0 - 100 degrees	0.149
Tensile strength (distilled calcium), kilograms per square millimeter	4.4
Elongation (distilled calcium), percent	53
Hardness by Brinell	17
Electrode potential vis-a-vis hydrogen electrodes, volts	-2.2
Electrochemical equivalent, grams per ampere-hour	0.747

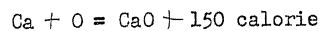
At the present time, three allotropic varieties of metallic calcium are known to exist:  $\alpha$ ,  $\beta$  and  $\gamma$ , which differ from each other with respect to crystalline formation. Type ( $\alpha$ ), existing under normal temperatures, is converted at 300 degrees Centigrade to type ( $\beta$ ), which in turn becomes type ( $\gamma$ ) at 450 degrees Centigrade.

Metallic Calcium may be subjected to various kinds of mechanical treatments; moreover, the very pure metal, produced by sublimation in a vacuum, is extremely pliable. Elongation during tensile strength tests is very large and exceeds corresponding figures for aluminum, magnesium and lead, as is evident from the following figures:

	Ca	Pb	Al
Tensile Strength, kilograms per square millimeter	4.4	1.8	6
Elongation, percentage	53	43	25

Specific electrical conductivity of calcium is lower than that of silver, copper, gold, aluminum and is equal to 45.1 percent of the electro-conductivity of silver.

In the electromotive series, calcium is found among the most electronegative metals (electrode potential 2.2 volt), which fact is responsible for its high chemical activity. The reaction of calcium with oxygen is highly exothermic.



The metal tarnishes easily on exposure to air and takes on coating of porous oxide. At 300 degrees Centigrade pulverized metal burns in oxygen, and, if heated above 300 degrees Centigrade, calcium will combine with nitrogen producing hydride  $\text{Ca}_3\text{N}_2$ . At 915 degrees, calcium with hydrogen, forms hydride ~~CaH~~  $\text{CaH}_2$ . Calcium decomposes water at low temperatures, driving out hydrogen; and in a humid atmosphere, the

metal is covered with a layer of hydroxide.

It is necessary to point out that calcium containing many impurities, is subject to very intense corrosion; however, sublimated metal is characterized by considerable chemical stability and remains practically unchanged in concentrated solutions of caustic alkalis.

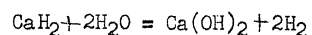
Nevertheless, even the sublimated calcium is easily affected by the action of dilute acids and alkalis.

The fields of application of calcium stem primarily from the metal's high chemical activity.

Calcium's ability to combine vigorously with all gases permits use of the alkaline earth in creating a high vacuum for the industrial separation of impurities from argon and also as a dehydrating agent for organic liquids (for example, alcohol).

Calcium hydride  $\text{CaH}_2$  is used for the transportation of hydrogen in this combination. In this case, the weight of hydrogen is 9.5 percent of the transported load, as against 0.9 percent when compressed hydrogen is shipped in cylinders.

During the production of hydride, metallic calcium is heated in an atmosphere of hydrogen. For the separation of hydrogen, hydride is treated with water.



In metallurgy, calcium is used as a reducing agent and an alloy component. As a reducing agent in the metallurgy of lead, calcium has the quality of eliminating not only all traces of aluminum, antimony and copper, but also of removing bismuth completely - a problem difficult to solve by other methods.

The advantage of using calcium as a reducing agent for copper is that, in contrast with silica, it increases the mechanical properties of copper, without lowering its electrical conductivity.

Addition of calcium to aluminum increases the electrical conductivity of the latter, at the expense of changing silica into silicide.

Calcium is an excellent reducing agent and degasser for steels and cast iron, eliminating completely sulphur and phosphorus; it is also used as a reducing agent in the production of such metals as chromium, uranium and thorium from their oxides.

Calcium has found broad application in lead alloys as a bearing metal, ~~an~~ an alloy of lead with 0.3-0.5 percent, Ca. The latter forms large solid crystals of  $Pb_3Ca$  in the malleable lead base.

A lead alloy containing 0.04 percent Ca, due to its toughness and resistance to corrosion, as compared with pure lead, may be used for the manufacture of cable sheathing.

#### 114 - Technology of Production of Metallic Calcium.

Developing methods of production of metallic calcium was approached from two directions: chemical reduction and electrolysis of fused calcium salts. However, the latter method has been industrially accepted.

The production of metallic calcium by the electrolysis of fused chlorides was first achieved by Mathieson in 1855. Industrial development of the method belongs to Rathenau and Zutter (1896).

The fused electrolyte used in the production of metallic calcium consists of a mixture of  $CaCl_2$  and  $CaF_2$  or mainly of pure anhydrous calcium chloride.

The production of the latter from hydrated salt ( $CaCl_2 \cdot 6H_2O$ ) due to its hydrolysis during dehydration and formation of calcium oxide, presents considerable difficulties. To avoid these, the dehydration of hydrated salt is conducted in the presence of ammonium chloride or in an atmosphere of hydrogen chloride.

On contact with air, the melted electrolyte is enriched with basic salts, and thus becomes viscous and less electro-conductive. This makes

it necessary to change the electrolyte in the operating bath from time to time.

However, the electrolyte, enriched with basic salts, is capable of dissolving up to 17 percent metallic calcium, thus causing considerable loss of metal.

The decomposition voltage of calcium chloride at a temperature of 800 degrees (Centigrade) is 3.24 volt. Pure anhydrous calcium chloride melts at 780 degrees, and metallic calcium at 800 degrees. However, since calcium heated over 800 degrees readily ignites on contact with air, the working temperature of the electrolytic process remains within very narrow limits.

As mentioned above, the difficulty in the production of calcium is the high solubility of the metal in the electrolyte. Therefore, calcium is obtained not in liquid form but in the form of rods gradually accumulating on the vertical cathode of contact in the same manner as in the production of beryllium. (Figure 211: Electrolyzer for the production of Metallic Calcium.)

Figure 212 shows the exterior of an industrial bath for the production of metallic calcium. The carbon or graphite walls of the electrolyzer serve as an anodic surface for the deposit of chlorine which is drawn off through the gas pipes. The electrolyte surface is in contact with iron cathodes, which gradually rise with the accumulation of calcium rods.

The process leading to the formation of calcium rods is achieved at a cathode current density of 50-100 amperes per square centimeter and electric current consumption of 30,000-50,000 kilowatt hours for one ton of calcium.

Theoretically, to obtain 1 kilogram of calcium, 2.76 kilograms of  $\text{CaCl}_2$  is required, but in practice 4-5 kilograms of the latter are used

to produce one kilogram calcium.

The metallic calcium rods obtained by electrolysis contain considerable amounts of the electrolytic components. Therefore, this metal is first melted in an enclosed container and then cast into ingots.

However, the remelted calcium contains a number of metallic impurities (iron, aluminum, sodium, silicon) as well as some components of the electrolyte. Calcium content is 98.4-98.6 percent.

To obtain pure metal, electrolytic calcium (like magnesium) is sublimated in a vacuum at a temperature of 800 degrees.

Such an installation for the sublimation of calcium is shown in Figure 213.

The sublimation of calcium results in a very pure metal (containing for example 99.3 percent Ca; 0.02 percent Fe and 0.14 percent Si) which, as we mentioned before, is highly resistant to corrosion and is pliable.

Melted calcium chloride may also be subjected to electrolysis using cathodes of fused metals--lead, zinc and others. Thus, one obtains directly by electrolysis, alloys of calcium with corresponding metals.